NON INTRUSIVE CHEMICAL SPECIES MEASUREMENTS DURING PREIGNITION REACTION PROCESSES

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13. ABSTRACT (Maximum 200 words)

This ASSERT program involved development and application of laser diagnostic techniques as part if a research program at Drexel University to study the oxidation and ignition characteristics of hydrocarbon fuels and their mixtures. The research program entailed mechanistic studies examining the overall ignition of pure single component fuels and fuel blends. Gas chromatography, gas chromatography/mass spectrometry, and gas chromatography/Fourier Transform Infrared Spectrometry (FTIR) analyses were used to determine the stable reaction intermediates and products associated with the preignition oxidation of these fuels. Development and application of spectroscopic diagnostics to permit in situ measurement of selected table and radical species also was successful. Associated in-house and collaborative modeling efforts were used to model and predict relevant ignition and emission characteristics.

We have investigated the oxidation of pure hydrocarbons and hydrocarbon blends in our various combustion systems, with emphasis on the effects of elevated pressure using our pressurized flow reactor (PFR) facility. Detailed experimental data were generated from the PFR for use in associated kinetic modeling work. We continued to develop and extend both detailed and reduced chemical kinetic models. Also, we collaborated with other laboratories to develop the insitu measurement capabilities using degenerate four wave mixing (DFWM) and cavity ringdown laser absorption spectroscopy (CRLAS).

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ABSTRACT

A research program to study the oxidation and ignition characteristics of hydrocarbon fuels and their mixtures has been conducted at Drexel University. The program started in January 1993 with the awarding of a research grant through the Army Research office (Grant No. DAAH04-93-6-0042, Project No. 30782-EG) and was completed in January 1998. This program was augmented with an associated ASSERT award (Grant No.DAAH04-93-G-0145; Project No. 32170-EG-AAS) which ran from 5/1/93 through 10/31/96. This report summarizes the overall progress and highlights the ASSERT activity.

The research program entailed mechanistic studies examining the oxidation chemistry of single-component hydrocarbons and ignition studies examining the overall ignition of pure single component fuels and fuel blends. Gas chromatography, gas chromatography/mass spectrometry, and gas chromatography/Fourier Transform Infrared Spectrometry (FTIR) analyses were used to determine the stable reaction intermediates and products associated with the preignition oxidation of these fuels. Development and application of spectroscopic diagnostics to permit in situ measurement of selected table and radical species also was successful. Associated in-house and collaborative modeling efforts were directed towards developing detailed and reduced chemical mechanisms that were used to model and predict relevant ignition and emission characteristics.

We have investigated the oxidation of pure hydrocarbons and hydrocarbon blends in our various combustion systems, with emphasis on the effects of elevated pressure using our pressurized flow reactor (PFR) facility. Detailed experimental data were generated from the PFR for use in associated kinetic modeling work. We continued to develop and extend both detailed and reduced chemical kinetic models. Also, we collaborated with other laboratories to develop the situ measurement capabilities using degenerate four wave mixing (DFWM) and cavity ringdown laser absorption spectroscopy (CRLAS).

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I. INTRODUCTION

A. Motivation

Federal agencies whose goal is to provide improvements in mobility and transportation face two closely associated combustion related problems over the next decade. The first, deteriorating and variable quality of fuels, was identified in the 80's (AGARD, 1982) and was highlighted during the recent military efforts in the Middle East. The second is the difficulty with balancing increased improvements in engine efficiency with the need for reduced engine emissions. A primary facet of both the fuel quality and emissions problems is to determine what conditions are necessary to achieve reliable ignition of the fuel. Difficulties with ignition are responsible for several engine problems, notably: knock in spark ignition engines, misfire, and cold start in diesel engines. Henein (1976) and Henein et al. (1992) highlighted the importance of the chemistry by demonstrating that the chemical processes are rate controlling during the delay period in diesel ignition. High emissions are also produced during the initial start-up of a combustion engine (Kamimoto and Kobayashi, 1991).

The compression ignition process is complex and involves preignition reactions which lead up to the point of autoignition. This is the point at which energy is liberated at a sufficient rate to sustain combustion in the absence of an external energy source, and is characterized by rapid rates of pressure and temperature rise. The tendency of a fuel to autoignite is directly related to the manner in which it undergoes oxidation and is determined by its chemical structure. In order to gain insight into the autoignition characteristics of hydrocarbon fuels, it is necessary to understand the chemistry of oxidation, especially the reactions that occur prior to autoignition. The oxidation chemistry determines the heat release rate, the reaction intermediates, and the ultimate products of combustion. The large number of concurrent and competing chemical reactions which involve a correspondingly large number of chemical intermediate species results in a very complex mechanism for the oxidation chemistry. This is the case even for small, single component fuels such as methane, and becomes exponentially more complex as the size of the fuel molecule increases. Consequently, attempting to understand the detailed chemistry of distillate fuels, which are multicomponent blends of a variety of relatively high molecular weight hydrocarbons, from direct studies of the complex fuels has proven to be untractable.

An approach which will be successful for both the predicton of ignition quality and the assessment of autoignition chemistry involves testing individual fuel components and simple fuel blends in laboratory scale chemical reactors. With this approach, the physical factors influencing the ignition process can be controlled much more carefully than in an engine, and ignition quality can be evaluated solely in terms of the chemical effects of the fuel components on the ignition process. Single fuel components representing the different classes of hydrocarbons within a

distillate fuel, such as alkanes, alkenes, and aromatics, can be blended at different ratios and tested in order to develop an understanding of how the different classes of hydrocarbons interact and which control the ignition behavior. Such studies can lead to the development of a method for predicting the ignition behavior of fuels, without extensive engine testing, based on knowledge of their composition. In view of this, a research program to study the oxidation and ignition characteristics of large hydrocarbon fuels and their mixtures has been conducted at Drexel University. The program started in January 1993 with the awarding of a research grant through the Army Research Office (Grant No. DAAH04-93-G-0042; Project No. 30782-EG), and included efforts under an associated AASERT award (Grant No. DAAH04-93-G-0145; Project No. 31270-EG-AAS). This final project report documents our activities on this ARO program which was completed in January 1998. The AASERT activities are the ones associated with developing and applying laser diagnostic techniques (identified by * where appropriate).

B. Objectives

The objectives defined for this study were to:

(1) obtain kinetic information in the low and intermediate temperature ranges (600-1100 K) over a range of pressures (up to 20 atm) for the oxidation of pure hydrocarbons

(2) determine the synergistic and antagonistic effects for mixtures of full boiling range fuel components;

(3) develop detailed and reduced chemical mechanisms which can model the progress of these reactions over the experimental range of conditions for use in predicting ignition and emissions characteristics; and

(4) * develop and apply new laser diagnostic techniques for species measurements in order to facilitate this work.

C. Methodology

The methodology of the program was to perform bench scale tests on single component, pure fuels and simple mixtures of pure fuels. The fuels were branched and straight chain aliphatics and aromatics, which are representative of components in distillate fuels and gasolines. The experiments were carried out over a range of reaction conditions which are representative of actual engine conditions prior to and during the ignition process. A pressurized flow reactor and a static reactor were used in this study. Gas chromatographic, and Fourier Transform Infrared

Spectrometric (FTIR) techniques were developed to measure the stable reaction intermediates and products associated with the oxidation of these fuels. Results from these studies were used to provide kinetic and mechanistic information, to formulate hypotheses on autoignition mechanisms, to determine the relative effects of the various classes of components within multicomponent fuel mixtures, and to validate combustion models which can be used in the design and evaluation of engines.

* Two in-situ measurement techniques were developed and evaluated during this program. A novel, tilted beam version of degenerate four wave mixing (DFWM) was characterized and found to provide an order of magnitude increase in signal to noise ratio. Unfortunately, DFWM still lacks the sensitivity required to measure the important HO_2 radical in our reaction systems. In collaboration with Sandia National laboratories, we established a unique infrared cavity ringdown laser absorption spectroscopy (CRLAS) diagnostic which may be capable of measuring HO_2 and RO_2 in our reactor systems.

II. RESEARCH PROGRAM

An overview of the research activities carried out as part of our ARO research program is given in Section A, experimental facilities and procedures are discussed in section B, and a discussion of the specific research accomplishments for this program is provided in Section C. Our reports, publications and presentations currently completed are listed in Section D. A list of the scientific personnel and degrees awarded during this period are listed in Section E.

A. Research Overview

This research program examined the oxidation and ignition characteristics of hydrocarbon fuels at elevated pressures (up to 20 atm), with an emphasis on developing relevant high pressure kinetic and mechanistic information in the low and intermediate temperature regimes (650-1100 K). Significant progress was made in all of the identified task areas, with our most recent efforts directed towards the experimental investigation of the oxidation of pure hydrocarbons and hydrocarbon blends at elevated pressures, development of *in situ* laser diagnostic techniques including degenerate four-wave mixing (DFWM) and cavity ringdown laser absorption spectroscopy (CRLAS), and the prediction and validation of mechanisms relevant to the preignition chemistry of hydrocarbons and hydrocarbon mixtures. This work provided important new results elucidating the effects of pressure on hydrocarbon oxidation and ignition, as well as a number of key research issues (such as the centrality of coupled reaction paths in HC reaction systems). These results are pointing the way for future research efforts that will lead to a comprehensive understanding of fuel factors and physical effects on the oxidation and ignition process.

The primary experimental efforts in this research program were focused in two areas: studies of hydrocarbon oxidation; and development of optical measurement techniques. The hydrocarbon oxidation work included: studies with C4 and C5 hydrocarbons and their blends in the pressurized flow reactor facility (PFR); and studies of n-pentane, 1-pentene, and their blends in the static reactor (SR). The optical measurement technique development effort has included: implementation of an on-line, FTIR-based, multiple species quantification technique; and implementation and enhancement of two laser diagnostics (degenerate four-wave mixing and cavity ringdown laser absorption spectroscopy).

B. Experimental Facilities and Procedures

The facilities and operating procedures used in this study have been described in detail elsewhere and the reader is referred to appropriate references below. However, brief summaries are included here.

The pressurized turbulent flow reactor is designed for operation up to 1100 K and 20 atm (Koert, 1990; Koert and Cernansky, 1992). The reactor test section is heated and lined with quartz in order to provide an adiabatic reaction zone free from wall effects. The gaseous fuel stream is heated and mixed with the preheated oxidizer in an opposing jet annular mixing nozzle. Samples of the reacting gases are withdrawn from the reactor midway between the reactor center-line and the reactor wall at variable axial locations with a glass-lined, water-cooled gas sampling probe. Control of the probe position is facilitated by the use of a stepper motor driven linear motion positioning table. Extracted gas may be directed to a variety of permanent gas analyzers for CO, CO_2 and O_2 concentration measurements, or stored in a heated storage unite capable of holding 15-10 cc gas samples at a typical pressure of 0.2 MPa. The heated sample storage unit was designed (Euchner, 1980) to prevent chemical changes to the product species contained in the sample. These samples were then analyzed on a gas chromatograph (GC). During this study, a Fourier Transform Infrared (FTIR) spectrometer was connected to the gas sampling probe so that on-line measurement of samples was possible (Wood, 1994; McCormick, 1994). This on-line system was applied extensively to investigate the oxidation of C4 and C5 alkanes, alkenes and their blends and NO/1-pentene mixtures (Wood, 1994; McCormick, 1994; Prabhu et al., 1996).

An existing static reactor system was available for the examination of low pressure ignition. This system has been used in previous studies on ignition behavior of high molecular weight hydrocarbons such as dodecane and tetralin (Wilk et al., 1985b, 1987b). It has also been used to study the detailed chemistry of lighter C3 and C4 hydrocarbons (Wilk et al., 1985a, 1986, 1987a, 1995; Addagarla et al., 1987; Prabhu et al., 1996). The static reactor system consists of a 1.4 liter cylindrical pyrex reaction vessel located inside a temperature controlled compartment. The system is equipped with associated instrumentation for monitoring and recording the pressure and temperature as the reaction progresses. For gaseous fuels, the reactants are premixed in a separate mixing vessel after which the homogeneous fuel/oxidizer mixture is admitted into the reaction vessel by way of a solenoid valve. For liquid fuels, a prechamber is used to vaporize the fuel in a nitrogen bath before mixing. During this study, the oxidation of n-pentene and 1-pentene/n-pentane blends was examined (Kumar, 1994; Prabhu, 1994).

* The in -situ diagnostic component of this research was focused on the development and application of two specific techniques: degenerate four-wave mixing (DFWM) and cavity ringdown laser absorption spectroscopy (CRLAS). DFWM was shown to have excellent spatial and

temporal specificity which makes it suitable in combustion environments with high temperatures and species concentrations, such as atmospheric-pressure flames. However, the minimum detection sensitivity of DFWM is severely limited compared to other techniques due to a nonlinear dependence on various molecular properties. CRLAS has a linear dependence on the parameters contained in Beer's law and can therefore detect weakly absorbing species which are inaccessible to DFWM. However, its path-integrating nature limits applications to one-dimensional systems, such as flat flames, and static and flow reactors. As such, these two methods can be considered complimentary in nature and have a large range of potential applications.

C. Specific Research Accomplishments

a. Upgraded the pressurized flow reactor system with the addition of a liquid flow controller and an auxilliary heater.

   In order to study higher boiling point fuels at elevated pressures, a method for metering liquid fuels was required. A controller has been developed to deliver liquid fuels into our pressurized flow reactor system which can operate at pressures between 2 and 20 atm. We have also added an auxilliary air heater to allow the flow reactor to reach reaction temperatures of 1100 K.

b. Developed a multiple species quantification technique using a Fourier Transform Infrared (FTIR) spectrometer.

   An on-line FTIR analysis system was added to the pressurised flow reactor facility. The system included a heated sample cell which is continuously filled with the extracted sample. A rapid speciation technique was developed to analyze multicomponent gas samples using FTIR spectroscopy and was used to measure species evolution profiles for C4 and C5 oxidation studies. The concentrations of all stable species were determined by linear least squares fitting procedures except for carbon monoxide, carbon dioxide, and water which were measured using nonlinear calibration curves.

c. Experimentally mapped the transition between low and intermediate temperature reactivity at high pressure for typical fuel component structures, a straight chain C4 alkane (n-butane) and a branched chain C4 alkane (isobutane).

   Detailed species measurements indicated a shift in the product yields between low temperature and intermediate temperature reactivity (indicated by a temperature interval of reduced reactivity, called the negative temperature coefficient (NTC) region) during the oxidation of n-butane and isobutane. Oxygenates were favored at low temperatures while olefins were the dominant products in the NTC region. This is caused by an exchange in dominance between alkylperoxy and hydroperoxy radical reaction paths. Alkylperoxy radicals lead to reactions that favor the formation of oxygenated hydrocarbons, while the hydroperoxy radical leads to the formation of olefins. Results of the isobutane oxidation indicate that the rate of excited isobutylperoxy radical, $RO_2^{*\bullet}$, generation is a function of initial fuel concentration, pressure, dilution, equivalence ratio, and temperature. Results also indicate that the conversion of $RO_2^{*\bullet}$ to stable products is only a function of temperature and, to a lesser degree, extent of reaction. These reactions appear to be

independent of changes in initial fuel concentration, pressure, equivalence ratio, and dilution.

d. Investigated the effect of hydrocarbon structure and saturation on oxidation by studying the oxidation mechanism of 1-butene and trans 2-butene (conjugate alkenes to the C4 alkanes).

Experiments conducted with 1-butene suggest that it does not initiate reactions at temperatures below 850 K. In mixtures with n-butane, 1-butene does react at these temperatures and the product distributions suggest that the radicals which attack 1-butene predominately interact with the alkane end of 1-butene. Experiments conducted with trans 2-butene suggest that it begins to initiate reactions at 740 K. Mixtures of n-butane and trans 2-butene show significant differences in reactivity as compared to pure n-butane and suggest that trans 2-butene inhibits low temperature reactivity. It is felt that the changes are due to trans 2-butene's lack of an alkane section, which implies that trans 2-butene must react as an alkene. Differences in alkane and alkene oxidation chemistry at low temperatures explain the drop in reactivity. It was observed that different reaction steps control the oxidation of 1-butene and trans 2-butene and similar reaction steps control the oxidation of n-butane and 1-butene.

e. Investigated reaction chemistry significant to autoignition and engine knock in a study of n-pentane oxidation in the Drexel static reactor facility.

Experiments have been conducted in the static reactor to study n-pentane oxidation at equivalence ratios of 0.36 and 0.8. These experiments were conducted over the temperature range 548 to 742 K and at pressures from 200 to 400 torr. Profiles of temperature, pressure and concentration of product species with respect to time were obtained. The experimental results showed a region of cool flame behavior between 573-648 K, and onset of negative temperature coefficient behavior at 673 K. These results indicate that the reaction mechanism is different over these temperature zones.

f. Studied the oxidation of larger sized components of full-boiling fuels at elevated pressures (n-pentane).

Lean n-pentane oxidation was examined at 4, 8 and 12 atm pressures in the PFR. Strong NTC behavior was observed beginning at 720 K, and is attributed to the same shifts in radical dominance as occurs with the smaller alkanes. Very high yields of oxygenated hydrocarbons were observed in the NTC region primarily as a result of secondary oxidation of C5 alkenes. Also, formaldehyde and carbon monoxide formation exhibited a significant pressure effect, possibly due to enhanced importance of the "Waddington" mechanism with increasing pressure. Moreover, n-pentane was consumed faster with increasing pressure. These results and general system behavior present a significant challenge to the development of a comprehensive chemical kinetic model of preignition behavior of large hydrocarbons.

g. Studied 1-pentene oxidation in the static reactor system and evaluated the oxidation mechanism of olefins based upon these results and on preliminary 1-pentene work in the PFR.

1-Pentene is the conjugate olefin to n-pentane, so it is of considerable interest in elucidating fuel composition and structure effects. With this olefin, changes in product distribution indicated a transition in the chemistry between the low and intermediate temperatures in the region of the NTC behavior; this was interpreted using a mechanism which describes the main reaction paths and shifts. Increasing density increased the overall formation of formaldehyde and decreased the overall formation of carbon monoxide during C5 alkene oxidation. The "Waddington" mechanism was presented as a possible explanation for the

increase in formaldehyde production. High yields of propionaldehyde are believed to be due to decomposition of alkylhydroperoxide radical.

h. Investigated the oxidation of a C5 alkene/alkane blend (1-pentene/n-pentane) in the low and intermediate temperature regions.

Studies of a n-pentane - 1-pentene blend in the static reactor indicated that in a mixture the two components reacted intramolecularly through a common pool of small labile radicals such as OH, H and HO_2. At low temperatures, the alkene preferentially reacted with the radicals and diverted the reaction into the slower alkene chain, reducing the reactivity of the alkane. In the region of NTC and just beyond, where the alkane is relatively unreactive, the n-pentane acted as a radical trap for some of the radicals formed in the alkene reaction chain, thereby retarding the activity of the alkene. Based on these data a modified reaction mechanism was proposed.

i. Improved the kinetic mechanism for numerical modeling of the detailed chemistry of NTC behavior.

Numerical modeling of the detailed chemistry of NTC behavior has been carried out both in house and in collaboration with Dr. William Pitz and Dr. Charles Westbrook of Lawrence Livermore National Laboratories. The reactions found to have the greatest tendency to enhance the NTC behavior are: diperoxy radical decomposition reactions, hydrogen peroxide decompositions, and alkyl peroxy radical recombinations. Recent efforts have focused on the propane oxidation data at 10 and 15 atm from the Drexel PFR in order to include pressures significant to engine processes. In this particular activity, the collaboration was expanded to include QRRK calculations of unimolecular rate constants of the $R{\bullet}+O_2$ reactions of C_2 and C_3 hydrocarbons by Dr. Joseph Bozzelli of New Jersey Institute of Technology and Dr. Anthony Dean of Exxon Research and Engineering. Overall this effort has been able to reproduce the qualitative behavior of fuel consumption and some major reaction products.

j. * Detected the CN radical using laser spectroscopy (degenerate four wave mixing-DFWM).

Our development of DFWM techniques and applications for combustion studies has led to the first DFWM measurement of CN radical (using the $B^2\Sigma^+ - X^2\Sigma^+$ band). A Nd:YAG pumped dye laser optical system was used to measure (LIF and DFWM) CN in a H_2 / C_2H_2 / O_2 / N_2 / NO atmospheric-pressure premixed flame produced on a 25 x 0.5 mm water cooled slot burner. We estimate a minimum detectable quantity of approximately 6 x 10^{12} CN molecules/cm^3 for this technique. Continued development of such optical techniques will provide significant new tools for our fuel combustion studies.

k.* Improved DFWM signal to noise ratio (S/N) using the tilted backward pump beam geometry.

Tilting the backward pump beam in a degenerate four wave mixing (DFWM) application results in tilting the signal beam below the horizontal plane by an equal angle, allowing for increased signal collection and a significant decrease in scattered background light interference. The higher signal intensity for tilted-DFWM is due to the use of a high intensity mirror for signal collection. The scattered light was found to preferentially scatter in the horizontal plane, hence the lower noise level for the tilted DFWM geometry. The overall result is an order of magnitude increase in the DFWM signal to noise ratio (S/N).

This significant improvement in S/N will be useful in detecting radicals and other species that exist in low concentrations in preignition reaction regions and in flames.

l. Experimentally investigated the oxidation of 1-pentene (conjugate olefin to n-pentane) in the low and negative temperature coefficient (NTC) region in the PFR.

The experiments were conducted at elevated pressures (4, 6, 8 and 12 atm) and over the temperature range of 600-800 K. 1-Pentene showed alkane type behavior exhibiting low temperature reactivity and strong negative temperature coefficient behavior. An examination of the product distribution revealed that hydrogen abstraction reactions leading to allyl radicals are more important than radical addition to the double bond. This is in contrast to previous studies on terminal olefins where the addition route was proposed as the dominant fuel consumption pathway. We believe that, as molecules get larger, alkane type reaction behavior occurs at the end of the molecule away from the terminal olefin, and that this is the reactivity observed in our experiments.

m. Examined the effect of nitric oxide (NO) on hydrocarbon oxidation in the low temperature and negative temperature coefficient (NTC) region.

The effect of nitric oxide (NO) on hydrocarbon oxidation in the low temperature and negative temperature coefficient (NTC) region has been examined. In related engine studies, we have shown that typical residual NO concentrations can significantly enhance autoignition of a primary reference fuel blend of octane rating 92. Detailed experiments in our pressurized flow reactor with 1-pentene have shown a similar NO effect. Overall, small amounts of NO enhance reactivity at all temperatures, while larger amounts (> 350 ppm) reduce reactivity at low temperatures and enhance reactivity at higher temperatures, particularly in the NTC region. At low temperatures the chain terminating reaction between NO and OH has been used to explain the reduction in reactivity with high concentrations of NO. The enhancement of reactivity has been explained by the reaction of NO with hydroperoxy (HO_2) radicals producing relatively more reactive hydroxyl (OH) radicals. At any given condition the effect of NO is dependent on the balance between these chain terminating and chain propagating reactions.

n. Developed a pressure dependent kinetic mechanism for propane oxidation and compared it to experimental data from our pressurized flow reactor.

The detailed species evolution profiles generated from our experimental studies on propane oxidation at elevated pressures were used in the development of a kinetic model incorporating the low temperature and negative temperature coefficient chemistry. The experimental conditions range from 10-15 atm, 650-800 K, and were performed at a residence time of 200 ms for propane-air mixtures at an equivalence ratio of 0.4. Numerical simulations show that many of the key reactions involving propylperoxy radicals are in partial equilibrium at 10-15 atm. Major reactions in partial equilibrium include $C_3H_7 + O_2 = C_3H_7O_2$, $C.{}_3H_6OOH = C_3H_6 + HO_2$ and $C.{}_3H_6OOH + O_2 = O_2C_3H_6OOH$. The modeling results show propyl radical and hydroperoxy-propyl radicals reactions with O_2 proceed primarily through thermalized adducts, not chemically activated channels.

o. Developed a new reduced chemical kinetic model for prediction of preignition reactivity and autoignition of primary reference fuels.

Experimental data from the neat primary reference fuels (PRF's), 63 PRF and 87 PRF were used to develop a new reduced chemical model for predicting their major oxidation behavior. The model can predict ignition delay, preignition heat release, and the behavior of key chemical species including consumption of the fuel, formation of CO as a major oxidation

product, and production of other species classes. Experimentally observed negative temperature coefficient (NTC) behavior and charge density effects are properly predicted. This model represents a major improvement over other currently available ignition models. It appears that the model will be able to satisfactorily predict the major preignition oxidation behavior at low and intermediate temperatures with appropriate adjustments to the fuel specific rate parameters.

p. * Mapped cyanogen (CN) radical flame profiles using the DFWM technique.

The improved signal to noise ratio (S/N) of the tilted backward pump beam DFWM geometry has allowed for straightforward detection of the cyanogen (CN) radical, even though it is typically present in combustion systems in relatively low concentrations. As noted, the first such measurements were made using the $B^2\Sigma^+ - X^2\Sigma^+$ band in a H_2 / C_2H_2 / O_2 / N_2 / NO atmospheric-pressure premixed flame. Subsequently, we have used DFWM CN measurements to help characterize nitrogen chemistry in flames. Specifically, relative CN concentration profiles were measured for ten premixed C_3H_8 / N_2 / O_2 / NO atmospheric pressure flat flames at various equivalence ratios. It was found that the CN concentration profile is strongly dependent on equivalence ratio with a maximum amount produced for an equivalence ratio of 1.73. No CN formation was observed in fuel-lean flame conditions.

q. * Upgraded our dye laser system to measure polyatomic rovibrational bands in the near-infrared (1.00-1.65 mm)

This task was successfully accomplished by using the first Stokes stimulated Raman scattering technique in asingle-pass, open, pressurized, hydrogen-filled cell. This constituted the first such extension of a dye laser tuning curve to the near-infrared.

r. * Explored the feasibility of measuring radical polyatomic species using laser based techniques.

A collaborative effort was initiated with David Rakestraw's group at Sandia National Laboratory (Livermore, CA) to study the feasibility of measuring radical polyatomic species in high temperature / low pressure laminar flat flames using infrared laser absorption-based techniques, namely cavity ringdown laser absorption spectroscopy (CRLAS) and degenerate four-wave mixing (DFWM). Absolute absorption profiles were calculated for a number of radicals, including HO_2, CH_3, CH_2, and C_3H_3, based on known absorption cross sections (correcting for temperature-dependent partition functions) and molecular number densities predicted by chemical kinetic mechanisms published in the literature and the Miller-Bowman mechanism run at Sandia. It was found that the cross sections for polyatomic species diminish drastically in the high temperatures found in flames, due to an increased number of populated energy states. Hence, all these radicals (with the exception of CH_3) are weak absorbers (a maximum fractional absorption of < 10 ppm) in CH_4 and C_2H_2 low pressure flames and in C_3H_8 atmospheric pressure flames. HO_2 is a moderately strong absorber in lean formaldehyde flames, with a maximum fractional absorption of 120 ppm. The methyl radical was found to be a strong absorber in all systems, with a maximum of approximately 5000 ppm for a CH_4 flat flame. We concluded that CRLAS, with a detection limit of approximately 10 ppm, has the potential of measuring CH_3 under these conditions, but not the other radicals in the flames studied. DFWM, with a detection limit approximately two orders of magnitude less sensitive than CRLAS, has no apparent potential of measuring such weakly absorbing species in high temperature systems.

s. * Detected and quantified methyl radical (CH_3) in low pressure laminar flat flames using infrared cavity ringdown laser absorption spectroscopy (IR-CRLAS).

We successfully used (in collaboration with Sandia) infrared cavity ringdown laser absorption spectroscopy (IR-CRLAS) to detect and quantify methyl radical (CH_3) in stoichiometric and fuel-rich (ϕ=1.58) low pressure laminar CH_4 / O_2/ N_2 flat flames. This effort constitutes the first infrared measurement of a combustion-generated polyatomic radical in any high temperature environment. Five transitions in the ν_3 fundamental vibrational band near 3 mm were identified based on both experimental observations and theoretical calculations. The spectral congestion in the mid-infrared was found to be significant: approximately 40 resolvable absorption features were observed in a small spectral window ($\approx$ 2.5 cm^{-1}), some of which were identified to be due to CH_4, H_2O, C_2H_2, CO_2, and OH. The height-above-burner (HAB) temperature dependence for both flames was also determined via experimental N_2-CARS spectra. The resulting temperature profiles, in addition to cross section data in the literature, allowed for the quantification of the methyl flame data and comparison to predictions made by the Miller-Bowman chemical kinetic mechanism. It was found that the model accurately predicted the methyl HAB concentration profile for ϕ=1.0. For the fuel-rich case, the model over predicted both the amount and position of the maximum CH_3 concentration.

t. * Detected and quantified formyl radical (HCO) in low pressure laminar flat flames using visible cavity ringdown laser absorption spectroscopy.

We successfully used (also in collaboration with Sandia) visible cavity ringdown laser absorption spectroscopy to detect and quantify formyl radical (HCO) in low pressure laminar CH_4 / O_2/ N_2 flat flames. The visible *A-X* electronic band was chosen due to the availability of published line positions and absorption cross sections. The Q(8) line was chosen for monitoring and formyl HAB absorption intensity profiles were obtained for the low pressure flames described in the previous section. The Q(8) absorption cross section was temperature-corrected using the computer-fitted N_2-CARS data described above, and the experimental HAB absolute number density profiles for formyl were subsequently obtained. These experiments constitute the first *in situ* measurement of formyl HAB concentration profiles in any flame environment. The comparison of the formyl data to the Miller-Bowman calculated values was similar to that for methyl: satisfactory comparison for the stoichiometric flame but an over prediction of the position and maximum concentration of formyl radical.

u. Investigated neopentane and full boiling range fuel oxidation in our PFR facility.

Initial tests indicate a negative temperature coefficient behavior for neopentane. Detailed product distributions in low and intermediate temperature regimes have been measured using fourier transform infrared spectroscopy and non-dispersive infrared analysis. These data will contribute to our later kinetic modeling work. We have also recently generated comparable reactivity maps with industry standard fuels (ISF's) in the well characterized thermal and fluid environment of our PFR. The fuels examined in our work include RFA, RFB, 87 PRF, 92 PRF, a standard Ford test fuel, Indoline, and a simplified fuel mixture of aromatic, olefinic and saturated hydrocarbons (92 RON MIX). The negative temperature coefficient regimes of all these fuels have been mappped and accurately match our engine data for similar fuels. We have initiated a "group species analysis" for the ISF's, which will provide a data set for future kinetic modeling work.

D. List of all Publications and Technical Reports

Work accomplished as part of this research program has contributed to and resulted in the following publications, reports and presentations:

McCormick, T. W., Hori, M., Koert, D. N., Miller, D. L., and Cernansky, N. P., "Analysis of the Room Temperature Photolysis of Azomethane Using FTIR Spectroscopy," Paper No. WSSCI 93-012 presented at the Western States Section of the Combustion Institute 1993 Spring Meeting, Salt Lake City, UT, March 1993.

Prabhu, S. K., "The Oxidation of n-Pentane in the Low Temperature and the Negative Temperature Coefficient Regions,"M.S. Thesis, Drexel University, Philadelphia, PA, 1994.

Anand, A., "An Experimental Study of n-Butane Oxidation at Elevated Pressures in the Low and Intermediate Temperature Regimes," M.S. Thesis, Drexel University, Philadelphia, PA, 1994.

Kumar, A., "The Oxidation of 1-Pentene and a 1-Pentene - n-Pentane Blend in the Low and Intermediate Temperature Regions," M.S. Thesis, Drexel University, Philadelphia, PA, 1994.

Wood, C. H., "The Oxidation of n-Pentane and 1-Pentene in the Low and Negative Temperature Coefficient Regions," M.S. Thesis, Drexel University, Philadelphia, PA, 1994.

McCormick, T., "A Study of C4 Oxidation Chemistry using FTIR Spectroscopy," M.S. Thesis, Drexel University, Philadelphia, PA, 1994.

Anand, A., McCormick, T. W., Wood, C. H., Koert, D. N., Miller, D. L., and Cernansky, N. P., "Oxidation of n-Butane at Elevated Pressures," Paper No. WSSCI 94-013, presented at the Western States Section of the Combustion Institute 1994 Spring Meeting, Davis, CA, March 1994.

Koert, D. N., Miller, D. L., and Cernansky, N. P., "Experimental Studies of Propane Oxidation through the Negative Temperature Coefficient Region at 10 and 15 Atmospheres," Comb. Flame, 96:34-49, 1994.

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Prabhu, S., Wood, C. H., Miller, D. L., and Cernansky, N. P., "Effect of Nitric Oxide on 1-Pentene Oxidation in the Low and Negative Temperature Coefficient Regimes (600-800 K)," Paper No. 95S-050 presented at the Joint Technical Meeting of the CS/WS/MNSCI and AFRC, San Antonio, TX, April 1995.

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Gaffuri P., Faravelli, T., Garavaglia, E., Boldaniga, A., Garulo, F. J., Ranzi, E., and Cernansky, N. P., "Low Temperature Oxidation Mechanisms," Paper presented at the Italian National Section of the Combustion Institute Meeting, Naples, Italy, July 1995.

Wilk, R. D., Cohen, R. S., and Cernansky, N. P., "The Oxidation of n-Butane: Transition in the Chemistry Across the Region of Negative Temperature Coefficient," Industrial & Engineering Chemistry Research, 34: 2285-2297, 1995.

Koert, D. N., Pitz, W. J., Bozzelli, J. W., and Cernansky, N. P., "Chemical Kinetic Modeling of High Pressure Propane Oxidation and Comparison with Experimental Results," Paper No. WSSCI 95F-168, presented at the Fall Meeting of Western States Section of the Combustion Institute, Stanford, CA, October 1995.

Prabhu, S., Miller, D. L., and Cernansky, N. P., "Investigation of the Role of Nitric Oxide in Hydrocarbon Oxidation in a Single Cylinder Research Engine and a High Pressure Flow Reactor," Proceedings of The Third Asian-Pacific International Symposium on Combustion and Energy Utilization, Vol. I: 38-43, Hong Kong, December 1995.

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Gaffuri, P., Faravelli, T., Ranzi, E., Cernansky, N. P., Miller, D. L., d'Anna, A., and Ciajolo, A., "Comprehensive Kinetic Model for the Low Temperature Oxidation of Hydrocarbons," AIChE Journal 43(5):1278-1286, 1997.

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* Scherer, J. J., Aniolek, K. W., Cernansky, N. P., and Rakestraw, D. J., "Determination of Methyl Radical Concentrations in Methane/Air Flames by Infrared Cavity Ringdown Laser Absorption Spectroscopy," J. Chemical Physics, Vol. 107, pp. 6196-6203, 1997.

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Bhat, R. K., "The Effect of Nitric Oxide on the Oxidation of n-Pentane and Pressurized Flow Reactor Facility Upgrade", M.S. Thesis, Drexel University, Philadelphia, PA, 1998.

E. Research Personnel and Activities

This research project was coordinated under the supervision of Dr. Nichlolas P. Cernansky and Dr. David L. Miller as Co-Principal Investigators. They shared overall responsibility for conducting, directing, and reporting the various phases of research program. However, the primary responsibility for carrying out and implementing the details of the experimental and analytical aspects of the program fell on the graduate students and technical personnel supported by the project.

N. P. Cernansky - Co-Principal Investigator

D. L. Miller - Co-Principal Investigator

LIST OF STUDENTS GRADUATED

A. Anand - Research Assistant, M.S. Candidate (graduated April 1994)

A. Kumar - Research Assistant, M.S. Candidate (graduated June 1994)

C. Wood - Research Assistant, M.S. Candidate (graduated October 1994)

T. McCormick - Research Assistant, M.S. Candidate (graduated December 1994)

K. Kalim - Research Assistant, M.S. Candidate (graduated March 1995)

G. Srinavasan - Research Assistant, M.S. Candidate (graduated December 1996)

S. Tsay - Research Assistant, Ph.D. Candidate (graduated March 1996)

* K. Aniolek - Research Assistant, Ph.D. Candidate (graduated February 1998)

R. Bhat - Research Assistant, M.S. Candidate (graduated June 1998)

LIST OF STUDENTS EXPECTED TO GRADUATE

A. Khan - Research Assistant, M.S. Candidate (expected August 1998)

S. Wang - Research Assistant, Ph.D. Candidate (expected December 1998)

F. Report of Inventions

None.

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